COAL MINERALOGY, FORMS-OF-SULFUR AND IRON, AND COAL LIQUEFACTION PROPERTIES FOR THE ARGONNE PREMIUM COALS AND NINE KENTUCKY COALS.

Naresh Shah, Robert A. Keogh, Frank E. Huggins, Gerald P. Huffman, Anup Shah, Bhaswati Ganguly, and Sudipa Mitra, 233 Mining and Mineral Resources Bldg., University of Kentucky, Lexington, KY 40506.

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The eight Argonne Premium coal samples, augmented by nine Kentucky coals, were selected for this study of the relationship of mineral parameters and liquefaction behavior. Kentucky coals were screened from many coals as they exhibited high, low and intermediate values of rank, sulfur content and liquefaction yields. Table 1 lists the selected Kentucky coals and their carbon and sulfur analyses.

Liquefaction

Liquefaction experiments were carried out on all coals at 385 C with tetralin as solvent (1:1.5 coal/solvent ratio) and without any catalyst [1]. Microautoclaves (tubing bombs) were cold pressurized to 800 psi with hydrogen before heating to reaction conditions. Products of liquefaction were classified as: oils - pentane soluble; asphaltenes - pentane insoluble, benzene soluble; preasphaltenes - benzene insoluble, pyridine soluble; insoluble organic matter (IOM) - pyridine insoluble. Total conversion is defined as 100-IOM. Figure 1 is the bar chart showing the results of liquefaction reactions for all coals.

CCSEM

The mineral and inorganic species can act as catalysts or poisons during liquefaction depending on reaction conditions. It is, therefore, important to know the types of minerals present and how they are distributed in coal. Computer controlled scanning electron microscopy (CCSEM) is an excellent tool to rapidly characterize mineralogical information of coals [2]. Tables 2 and 3 list the mineralogical data obtained to date by CCSEM examination of Argonne and Kentucky coals. Two of the Argonne coals remain to be analyzed. With CCSEM, we can also determine average sizes and size distributions of the various minerals present in the coal. We are currently trying to correlate the pyrite surface area to the liquefaction conversion percentages.

It may be noted that "mixed silicates" account for a fairly large percentage of the mineral matter in these raw coal samples. This phase primarily includes clay minerals and quartz in juxtaposition to each other, perhaps in partings. This is illustrated by the ternary diagram in Figure 2. Here, each point represents a mineral feature identified in the CCSEM analysis that contains $\geq$90% of (K + Fe) + Al + S on the basis of its energy dispersive X-ray (EDX) spectrum. The composition is normalized to these four elements and plotted in a ternary representation, as shown. It is evident that there is a range of compositions extending between the quartz, kaolinite, and illite composition areas. It is these intermediate compositions that the coal mineral analysis (CMA) program identifies as mixed silicates.

Mössbauer Spectroscopy

Mössbauer spectroscopy is used to identify and quantify iron bearing phases present in the coals. [3,4]. Iron predominantly exists as pyrite, siderite or Fe-containing clay in coals. Mössbauer spectroscopy is the most accurate tool to quantify pyrite in coal and by using simple stoichiometric formula we can obtain the pyritic sulfur content of the coal. Table 4 lists the Mössbauer spectroscopy results for all coals. As it is clearly evident, the Argonne coals were in pristine condition and do not exhibit any pyrite oxidation.

However, some of the Kentucky coals, mainly those with high pyrite contents have undergone some minor oxidation that converts pyrite to sulfate form.

In order to examine the transformations of Fe-bearing minerals in coals as they undergo liquefaction and thereby assess the role of the inherent iron minerals as catalysts, the insoluble organic matter (IOM) of the Argonne Premium Sample coals were also investigated using Mössbauer spectroscopy. Figure 3 shows room temperature Mössbauer spectra of Illinois #6 coal before and after liquefaction treatment. In Illinois #6 coal, almost all Fe is present in the form of pyrite; after the liquefaction test, about 60% of the pyrite converts to pyrrhotite, while the remaining pyrite is unconverted. Under more severe conditions and/or longer periods of time, all of the pyrite would convert to pyrrhotite. In the Pocahontas #3 coal, iron is distributed among clays, siderite, and pyrite; however, in the Pocahontas #3 IOM, Fe in clays and carbonate remains unchanged whereas pyrite has been converted to pyrrhotite. As summarized in the Table 5 for the Argonne Premium Samples, this observation appears quite general: the Fe-bearing minerals, other than pyrite, do not appear to undergo significant transformation during liquefaction, whereas, some or all of the pyrite converts to pyrrhotite. It is likely that only Fe in the form of pyrrhotite is the primary catalytic species. Fe in the coal present in the form of clays is likely to be inactive.

<u>Sulfur XAFS</u>

It can be expected that different sulfur forms will behave differently under the same process conditions during liquefaction conditions and so it is important to identify the presence and reactions of each sulfur form under different conditions. The combination of Mössbauer and XAFS spectroscopy provides a unique approach to focus on both the different organic and inorganic forms of sulfur [5]. Figure 4 shows the sulfur K-edge XANES of three Argonne coals with pyrite removed. All three spectra are quite similar to each other indicating that the forms of sulfur present after pyrite removal are essentially the same in the three different coals. From our previous studies, we can assign various peaks in sulfur XANES to various forms of sulfur present in coals as follows: sulfidic sulfur (peak at 1.6 eV), thiophenic sulfur (peak at 2.6-2.8 eV), sulfoxide (peak at 4.5 eV), sulfone (peak at 9 eV) and sulfate (peak at 11 eV). We are currently trying to quantify the forms of sulfur present in these coals by curve fitting various features of the spectra and comparing the results to the data from standards.

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Table 1. Rank and total sulfur content of selected Kentucky coals

UKCAER Coal #	Seam	County	%C DAF	%S DAF
91864	WKY #9	Union	82.15	3.93
6398	Horton	Horton	85.33	0.86
2145	Peach Orchard #3	Magaffin	83.66	0.63
71302	WKY #6	Caldwell	82.50	3.37
3913	Stockton	Martin	82.34	0.75
2167	Cannel City	Magaffin	80.97	1.62
5416	Beaver Creek	Pulaski	74.45	13.92
71464	WKY #9	Henderson	79.44	3.84
71468	WKY #9	Muhlenberg	80.27	4.15

Table 2. Mineral Composition of Six Argonne Coals

	Wt% of Mineral Matter					
Mineral Species	Up. Fr.	Ill #6	Pitt #8	Poca #3	Bl. Cany	Lew Stoc
Quartz	5	9	12	4	4	10
Kaolinite	9	3	8	10	9	15
Illite	35	18	19	8	36	48
K-feldspar		<1		<1		
Chlorite	1			4		
Montmorillonite		<1	<1	<1	1	
Misc. Silicates	17	23	26	34	41	25
Pyrite	25	27	25	4	3	1
FeSO4					<1	
Gypsum	<1					
Chalcopyrite	<1			1		
Misc. Sulf.	1	1	1	<1	<1	<1
Halite (NaCl)				<1		
Apatite			<1			
Misc. Phosphates				<1		<1
Fe-rich		<1		<1	<1	<1
Calcite		8	1	7	2	
Ankerite				<1		
Mixed Carbonates	1	1	<1	5	1	<1
Ti rich		1	1	<1		1
Trace-rich	<1					
Qtz-Sulfur		1	<1			
Qtz-Pyrite	<1	<1		<1		
Sil-Sulfur	<1	3	2		<1	
Sil-Pyrite	<1	1	<1			
Al-rich				3		
Misc. Mixed	2	3	4	15	3	<1

Table 3. Mineral Composition of Kentucky Coals

Mineral Species	Wt% of Mineral Matter								
	6398	71468	2145	71302	3913	91864	2167	5416	71464
Quartz	3	8	11	7	10	13	6	1	8
Kaolinite	12	4	7	3	8	3	2		7
Illite	5	17	43	21	27	16	21	1	12
K-feldspar		<1		1	<1	1	1		
Chlorite	<1		<1	<1			1		
Montmorillonite	1		<1		<1	<1	<1		<1
Misc. Silicates	57	20	36	27	50	22	30	6	27
Pyrite	2	31		26		26	6	55	27
FeSO4		<1		<1		<1	<1	1	<1
Jerosite								1	
Gypsum									
Chalcopyrite									
Misc. Sulf.	<1	1		4	1	5	1	13	3
Halite (NaCl)									
Apatite							<1		
Misc. Phosphates									
Fe-rich	1						14	<1	
Calcite	1	11				<1			4
Ankerite									
Mixed Carbonates	1	1	<1			<1	11	<1	<1
Ti rich	3	<1	<1		<1	<1		<1	<1
Trace-rich			<1						
Qtz-Sulfur		<1		<1		1		1	1
Qtz-Pyrite		<1		3		1	<1	6	<1
Sil-Sulfur	5	3		2	2	5		2	5
Sil-Pyrite	<1	1	<1	2		1	<1	7	1
Al-rich						<1			
Misc. Mixed	10	3	1	5	2	5	7	6	5

Table 4. Mössbauer Data for Argonne Premium and Selected Kentucky Coals

Argonne Premium or Kentucky coals	Wt% pyritic sulfur	%Fe in			
		Clay	Siderite	Pyrite	Sulfate
Upp. Freeport	1.60	6	0	94	
Wyodak	0.13	0	26	74	
Illinois #6	2.14	3	0	97	
Pittsburgh #8	1.26	1	0	99	
Pocahontas #3	0.11	33	46	20	
Blind Canyon	0.25	0	28	72	
Lewis-Stockton	0.20	32	15	53	
Beulah-Zap	0.22	0	0	100	
91864	2.04			95	5
6398	0.03	61	16	22	
2145	0.15	57		43	
71302	1.86	5		88	7
3913	0.17	34		66	
2167	0.93	9	72	19	
5416	11.50			92	8
71464	1.87			96	4
71468	2.14			95	5

Table 5. Mössbauer Data for Argonne Coal IOMs

Argonne Premium Coal	%Fe in			
	Clay	Siderite	Pyrite	Pyrrhotite
Upper Freeport				100
Wyodak		21	42	37
Illionis #6			40	60
Pittsburgh #8			33	67
Pocahontas #3	38	50		12
Blind Canyon		31		69
Lewis-Stockton	32		31	37
Beulah-Zap			31	69

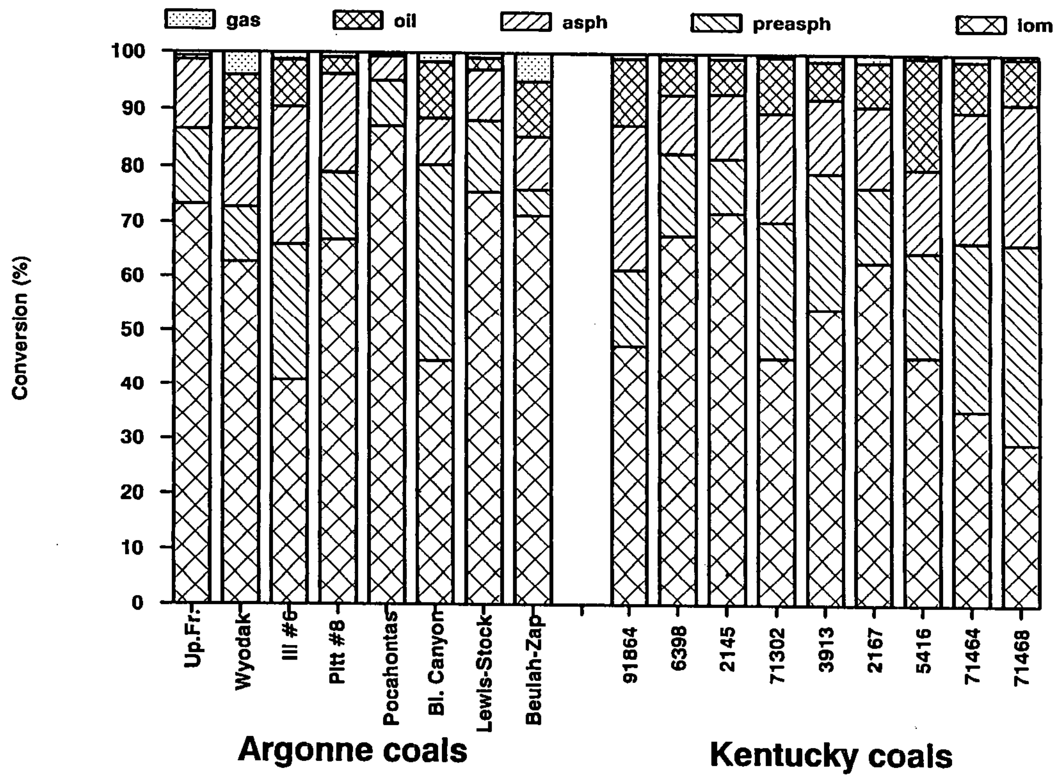

Figure 1. Liquefaction conversion percentages for Argonne Premium Coals and Kentucky Coals.

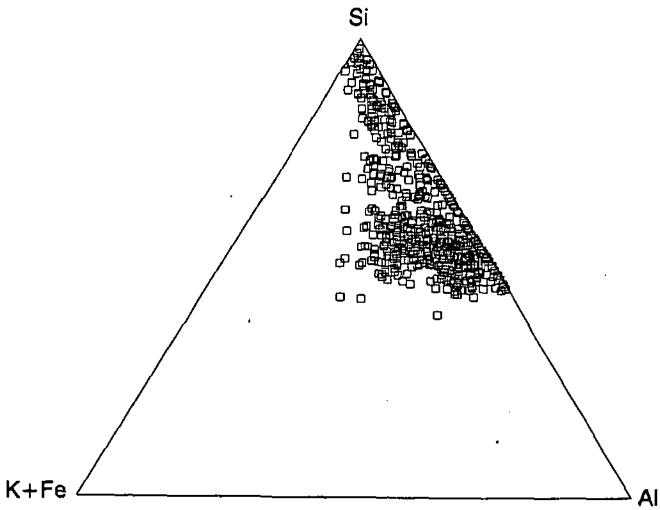

Figure 2. Ternary presentation of compositional data for quartz and clay minerals in Kentucky coal #3913.

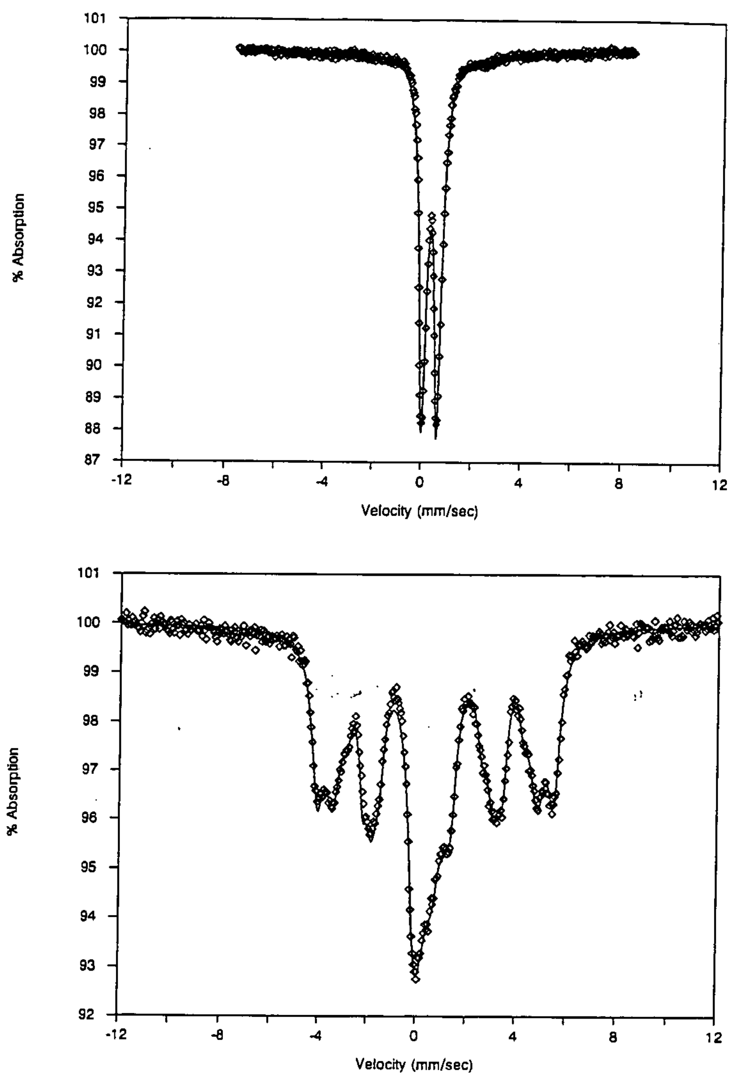

Figure 3. Mössbauer spectra of Illinois #6 raw coal (Top) and IOM (Bottom)

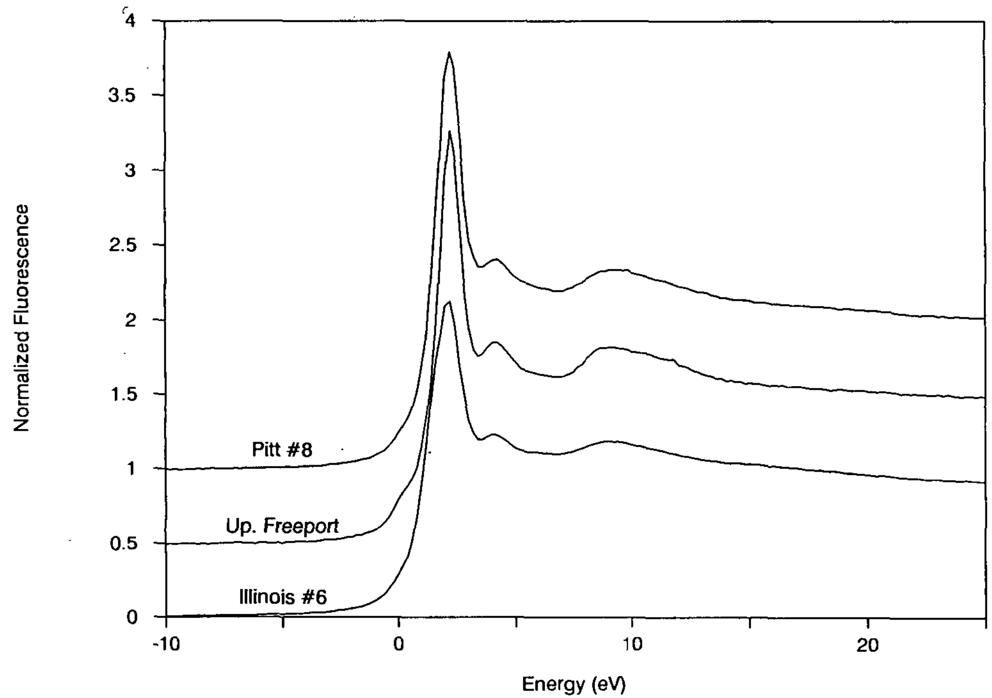

Figure 4. Sulfur K-edge XANES of three Argonne coals with pyrite removed.